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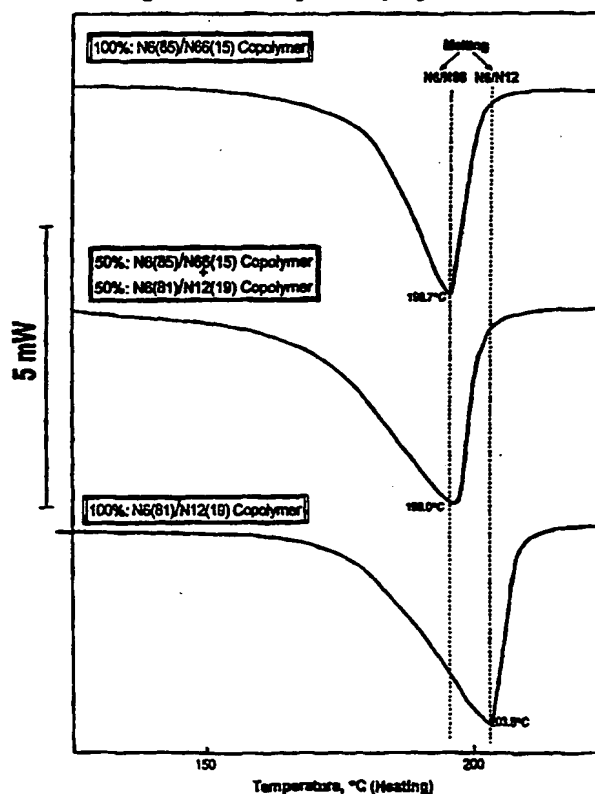
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(21) International Application Number: <b>PCT/US99/04692</b> (22) International Filing Date: <b>4 March 1999 (04.03.99)</b> (30) Priority Data: 09/038,201                      10 March 1998 (10.03.98) <b>US</b> (71) Applicant: <b>ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).</b> (72) Inventors: <b>KHANNA, Yash, P.; 2 Tree To Terrace, Morristown, NJ 07960 (US). PUTERBAUGH, Frank, Herbert, Jr.; 280 Hickory Corner Road, Milford, NJ 08848 (US). KUHN, William, Paul; 3909 Rachel Terrace, Pine Brook, NJ 07058 (US). SCHENA, Martin, James; 11 Bonnell Lane, Randolph, NJ 07869 (US).</b> (74) Agents: <b>CRISS, Roger, H. et al.; AlliedSignal Inc., Law Dept. (Amy Olinger), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).</b>		(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: **NYLON 6 OR 66 BASED COMPOSITIONS AND FILMS FORMED THEREFROM**

## (57) Abstract

Super-miscible blends of nylon copolymers are provided as well as multilayered film structures made therefrom. A nylon composition is a substantially uniform blend of at least one semi-crystalline copolymer I and at least one semi-crystalline copolymer II, wherein the proportion by weight of each copolymer I and copolymer II. The nylon compositions are extremely uniform, and have only a single melting point rather than individual melting points of the component nylon copolymer parts. Coextruded films of a layer of this nylon composition with an olefin containing copolymer are suitable for use as barrier films, such as aroma barrier films, which have reduced curl.

Melting Pattern Of Nylon Copolymer Blend Films



II is such that the composition has only one significant melting point; wherein copolymer I and copolymer II are as defined above.

5 The invention still further provides method for preparing a multilayered film structure which comprises coextruding a molten nylon composition film layer and a molten polyolefin layer attached onto at least one side of the nylon composition film layer, through a coextrusion die, wherein the polyolefin layer comprises at least one olefin containing polymer; wherein the nylon composition film layer comprises a substantially uniform blend  
10 of at least one semi-crystalline copolymer I and at least one semi-crystalline copolymer II, wherein the proportion by weight of each of copolymer I and copolymer II is such that the composition has only one significant melting point; wherein copolymer I and copolymer II are as defined above.

15 Such copolymers have improved anti-curling properties and a single melting point. According to this invention, nylon copolymers can be incorporated into a miscible blend in such a way that the resulting product is a one-component, homogenous material. The products of this  
20 invention are different from conventional blends in view of having only one melting point. The invention, in addition, allows one to incorporate multi-component copolyamides together with amorphous nylons, without observing non-homogeneity.

#### 25 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a graph of the melting pattern of copolymer blended films.

30 Figure 2 shows a graph of the melting pattern of other copolymer blended films.

Figure 3 shows a graph of the melting pattern of other copolymer blended films.

5            DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the practice of the present invention, a composition is prepared by melt blending at least one semi-crystalline copolymer which is a copolymer of a nylon A with a different nylon B, plus at least one semi-crystalline nylon copolymer which is a copolymer of nylon A with a different nylon C. The  
10       composition optionally also comprises a non-crystalline amorphous nylon copolymer D. The formed composition is determined to have only a single significant melting point. For purposes of this invention, having only a single significant point means that a second melting point, if one is observed, is no more than 35% of the main melting peak, more preferably no more than 20%  
15       of the main melting peak and most preferably no more than 10% of the main melting peak. The intensity of the second melting peak, if observed, is determined by known DSC methods. Such methods include analyzing a film to be tested after drying at 25 °C - 45 °C under vacuum for several hours. The intensity of the major and any minor peaks in DSC are determined by  
20       heat of fusion integrated over the melting ranges of the individual peaks. Preferably the composition has only one melting point and no other melting point at all.

The first component of the inventive composition is a semi-crystalline  
25       copolymer of nylon A with a different nylon B. Each of nylon A and nylon B may be either nylon 6 or nylon 66. Nylon 6 is also known as poly(caprolactam) and nylon 66 is also known as poly(hexamethylene adipamide).

30       The second component of the inventive composition is a semi-crystalline nylon copolymer which is a copolymer of nylon A plus at least one different

nylon C which may be nylon 9 - poly(9-aminononanoic acid), nylon 11 - poly(11-aminoundecanoic acid), nylon 12 - poly(12-aminododecanoic acid), nylon 46 or nylon 69.

5     The number average molecular weight of the nylon A/nylon B copolymer as well as the nylon A/nylon C copolymer may vary widely. Such are sufficiently high to form a free standing film but sufficiently low to allow melt processing of the blend. Such number average molecular weights are well known to those of skill in the film forming art and are usually at least  
10    about 5,000 as determined by the formic acid viscosity (FAV) method (ASTM D-789). In this method, a solution of 11 grams of aliphatic polyamide in 100 ml of 90% formic acid at 25°C is used. In the preferred embodiments of the invention, the number average molecular weight of nylon A as well as the nylon A/nylon B ranges from about 5,000 to about  
15    100,000, preferable from about 10,000 to about 60,000 and more preferably from about 20,000 to about 40,000.

The nylon composition may further contain an optional non-crystalline, non-crystallizable, amorphous nylon component D. Amorphous nylons  
20    are well known in the art and are available commercially. Amorphous nylons are typically prepared by the reaction of at least one diamine with at least two different diacids. The result is a non-homogeneous nylon having no determinable melting point. Amorphous nylons are available as Grivory 21 available from EMS of Switzerland and Zytel amorphous  
25    nylon from DuPont.

The proportion by weight of each of copolymer I and copolymer II is such that the composition has only one significant melting point. Preferably the amount of copolymer I ranges from about 75 % to about  
30    95% and the amount of copolymer II ranges from about 5 % to about 25 % based on the weight of the composition. More preferably the amount

of copolymer I ranges from about 90 % to about 93% and the amount of copolymer II ranges from about 7 % to about 10 % based on the weight of the composition.

5 Nylon A is preferably present in copolymer I in an amount of from about 70 percent to about 95 percent by weight and nylon B is preferably present in copolymer I in an amount of from about 5 percent to about 30 percent by weight of copolymer I. More preferably the amount of nylon A in copolymer I ranges from about 75 % to about 90 % and the amount  
10 of nylon B ranges from about 10% to about 25% by weight of copolymer I. Most preferably the amount of nylon A in copolymer I ranges from about 80 % to about 85 % and the amount of nylon B ranges from about 15% to about 20% by weight of copolymer I.

15 Nylon A is preferably present in copolymer II in an amount of from about 40 percent to about 95 percent by weight and nylon C is preferably present in copolymer II in an amount of from about 5 percent to about 60 percent by weight of copolymer II. More preferably the amount of nylon A in copolymer II ranges from about 50 % to about 80 % and the  
20 amount of nylon B ranges from about 30% to about 50% by weight of copolymer II. Most preferably the amount of nylon A in copolymer II ranges from about 50 % to about 65 % and the amount of nylon B ranges from about 35% to about 50% by weight of copolymer II.

25 When an amorphous nylon is included in the composition, it is present in the overall composition an amount of from about 1 % to about 5 %, preferably from about 2 % to about 4 % and more preferably from about 2 % to about 3 % based on the weight of the nylon composition.

30 The nylon composition may be formed by dry blending solid particles or pellets of each of the nylon components and then melt blending the mixture

at a temperature of at least the melting point of the higher melting point component. Typical melting temperatures range from about 175 °C to about 260 °C, preferably from about 215 °C to about 225 °C, and more preferably from about 220 °C to about 223 °C. Blending may take place  
5 in any suitable vessel such as an extruder, a roll mixer, or the like. Blending is conducted for a period of time required to attain a substantially uniform blend. Such may easily be determined by those skilled in the art. If desired, the composition may be cooled and cut into pellets for further processing, or it may be formed into films and  
10 optionally uniaxially or biaxially stretched by means well known in the art.

In the practice of the present invention, a multilayered film is prepared which is broadly composed of the nylon copolymer composition layer and a  
15 polyolefin layer attached to at least one side of the nylon layer by an optional adhesive. The adhesive preferably comprises at least one polyolefin having at least one functional moiety of an unsaturated carboxylic acid or anhydride thereof.

20 The polyolefins used herein include polymers of alpha-olefin monomers having from about 2 to about 6 carbon atoms and includes homopolymers, copolymers (including graft copolymers), and terpolymers of alpha-olefins. Illustrative homopolymer examples include ultra low density (ULDPE), low density (LDPE), linear low density  
25 (LLDPE), medium density (MDPE), or high density polyethylene (HDPE); polypropylene; polybutylene; polybutene-1; poly-3-methylbutene-1; poly-pentene-1; poly-4-methylpentene-1; polyisobutylene; and polyhexene.

30 Polyolefins such as polyethylenes are commonly differentiated based on the density which results from their numbers of chain branches per 1,000

carbon atoms in the polyethylene main chain in the molecular structure. Branches typically are C<sub>3</sub>-C<sub>8</sub> olefins, and which are preferably butene, hexene or octene. For example, HDPE has very low numbers of short chain branches (less than 20 per 1,000 carbon atoms), resulting in a relatively high density, i.e. density ranges from about 0.94 gm/cc to about 0.97 gm/cc. LLDPE has more short chain branches, in the range of 20 to 60 per 1,000 carbon atoms with a density of about 0.91 to about 0.93 gm/cc. LDPE with a density of about 0.91 to about 0.93 gm/cc has long chain branches (20-40 per 1,000 carbon atoms) instead of short chain branches in LLDPE and HDPE. ULDPE has a higher concentration of short chain branches than LLDPE and HDPE, i.e. in the range of about 80 to about 250 per 1,000 carbon atoms and has a density of from about 0.88 to about 0.91 gm/cc. Illustrative copolymer and terpolymers include copolymers and terpolymers of alpha-olefins with other olefins such as ethylene-propylene copolymers; ethylene-butene copolymers; ethylene-pentene copolymers; ethylene-hexene copolymers; and ethylene-propylene-diene copolymers (EPDM). The term polyolefin as used herein also includes acrylonitrilebutadiene-styrene (ABS) polymers, copolymers with vinyl acetate, acrylates and methacrylates and the like. Preferred polyolefins are those prepared from alpha-olefins, most preferably ethylene polymers, copolymers, and terpolymers. The above polyolefins may be obtained by any known process. The polyolefin may have a weight average molecular weight of about 1,000 to about 1,000,000, and preferably about 10,000 to about 500,000. Preferred polyolefins are polyethylene, polypropylene, polybutylene and copolymers, and blends thereof. The most preferred polyolefin is polyethylene.

In accordance with the present invention, suitable adhesives include modified polyolefin compositions composed of a polyolefin having at least one functional moiety of unsaturated polycarboxylic acids and anhydrides thereof. Polyolefins include any of those listed above.

Unsaturated carboxylic acid and anhydrides include maleic acid and anhydride, fumaric acid and anhydride, crotonic acid and anhydride, citraconic acid and anhydride, itaconic acid an anhydride and the like. Of these, the most preferred is maleic anhydride. The modified polyolefins  
5 suitable for use in this invention include compositions described in U.S. patents 3,481,910; 3,480,580; 4,612,155 and 4,751,270 which are incorporated herein by reference. The most preferred adhesive is a maleic anhydride modified ethylene  $\alpha$ -olefin copolymer which is also known as linear ultra low density polyethylene. The preferred modified polyolefin  
10 composition comprises from about 0.001 and about 10 weight percent of the functional moiety, based on the total weight of the modified polyolefin. More preferably the functional moiety comprises from about 0.005 and about 5 weight percent, and most preferably from about 0.01 and about 2 weight percent. The modified polyolefin composition may  
15 also contain up to about 40 weight percent of thermoplastic elastomers and alkyl esters as described in U.S. patent 5,139,878. The most preferred adhesive is Flexomer 1373 from Union Carbide which is a 10% maleic anhydride modified copolymer of ethylene and butene.

20 Each layer of the multilayer film structure can contain additives which are conventionally used in such films. Examples of such additives are pigments, dyes, slip additives, fillers, nucleating agents, plasticizers, lubricants, reinforcing agents, antiblocking agents, stabilizers and inhibitors of oxidation, thermal stabilizers and ultraviolet light stabilizers.  
25 Preferably, such may be present in an amount of about 10% or less based on the weight of the layer.

The multilayer films of this invention may be produced by conventional methods useful in producing multilayer films, including coextrusion,  
30 blown film and extrusion lamination techniques. In the most preferred method, the film is formed by coextrusion. Melted and plasticated



streams of the polyamide and polyolefin layer materials are fed into a co-extrusion die. While in the die, the layers are juxtaposed and combined, then emerge from the die as a single multiple layer film of polymeric material. Suitable coextrusion techniques are more fully described in  
5 U.S. patents 5,139,878 and 4,677,017 except coextrusion in this invention is conducted at from about 460 °F (238 °C) to about 510 °F (266 °C). Coextrusion techniques include methods which include the use of a feed block with a standard die, a multimanifold die such as a circular die, as well as a multimanifold die such as used in forming multilayer  
10 films for forming flat cast films and cast sheets. Alternatively the composition may be formed into a film using a conventional blown film apparatus.

An advantage of coextruded films is the formation of a multilayer film in  
15 a one process step by combining molten layers of each of the film layers of polyamide and polyolefin blend into a unitary film structure. Preferably the multilayers form an inseparable bond with one another. The term "inseparable bond" as used herein shall mean a bond strength of at least about 700 g/inch as determined by testing the film according to  
20 the procedure set forth in ASTM D-3359-90 and F88-85.

In order to produce a multilayer film by a coextrusion process, it is necessary that the constituents used to form each of the individual films be compatible with the film extrusion process. The term "compatible" in  
25 this respect means that the film-forming compositions used to form the films have melt properties which are sufficiently similar so as to allow coextrusion. Melt properties of interest include, for example, melting points, melt flow indices, apparent viscosity, as well as melt stability. It is important that such compatibility be present to assure the production  
30 of a multilayer film having good adhesion and relatively uniform thickness across the width of the film being produced. As is known in

the art, film-forming compositions which are not sufficiently compatible to be useful in a coextrusion process frequently produce films having poor interfacial lamination, poor physical properties as well as poor appearance. One skilled in the art can readily weigh the above-noted

5 compatibility in order to select polymers having desirable physical properties and determine the optimal combination of relative properties in adjacent layers without undue experimentation. If a coextrusion process is used, it is important that the constituents used to form the multilayer film be compatible within a relatively close temperature range in order to

10 permit extrusion through a common die. In the preferred embodiment when the nylon has a formic acid viscosity FAV of from about 120 to about 250 by ASTM D-789 and the polyolefin layer has a melt index of from about .5 to about 3 melt index units (MI) as determined by ASTM D-1238, the films will be compatible. That is, the nylon and polyolefin

15 layers will flow uniformly in the coextruder. The multilayered structure may have two, three or more layers of alternating nylon and polyolefin layers with the optional adhesive intermediate each layer.

Alternatively, the multilayer films of the present invention can be

20 produced by lamination whereby a multilayer film structure is formed from pre-fabricated film plies by methods which are well known in the art. The basic methods used in film laminating techniques are fusion, wet combining, and heat reactivating. Fusion, which is a method of laminating two or more film plies using heat and pressure laminated are comprised

25 of polymers that readily form interfacial adhesion. Wet combining and heat reactivating are utilized in laminating incompatible films using adhesive materials. Typically, laminating is done by positioning the individual layers of the inventive film on one another under conditions of sufficient heat and pressure to cause the layers to combine into a unitary

30 film. Typically the polyolefin and polyamide layers are positioned on one another, and the combination is passed through the nip of a pair of heated

laminating rollers by techniques well known in the art such as those described in U.S. patent 3,355,347. Lamination heating may be done at temperatures ranging from about 75°C to about 175°C, at pressures ranging from about 5 psig (0.034 MPa) to about 100 psig (0.69 MPa) for  
5 from about 5 seconds to about 5 minutes, preferably from about 30 seconds to about 1 minute.

The multilayer film, whether comprising a two, three or more layer structure, may be stretched or oriented in any desired direction using  
10 methods well known to those skilled in the art. Examples of such methods include those set forth in U.S. patent 4,510,301. Optionally, the film may be stretched uniaxially in either the direction coincident with the direction of movement of the film being withdrawn from the film forming apparatus, also referred to in the art as the "machine direction", or in as  
15 direction which is perpendicular to the machine direction, and referred to in the art as the "transverse direction", or biaxially in both the machine direction and the transverse direction. The films of the present invention have sufficient dimensional stability to be stretched at least 1.5 and preferably more than three times and more preferably from more than  
20 three times to about ten times in either the machine direction or the transverse direction or both. Typically for use in the present invention, the oriented film formed from the composition of the invention are preferably produced at draw ratios of from about 1.5:1 to about 6:1, and preferably at a draw ratio of from about 3:1 to about 4:1. The term  
25 "draw ratio" as used herein indicates the increase of dimension in the direction of the draw. Therefore, a film having a draw ratio of 2:1 has its length doubled during the drawing process. Generally, the film is drawn by passing it over a series of preheating and heating rolls. The heated film moves through a set of nip rolls downstream at a faster rate than the film  
30 entering the nip rolls at an upstream location. The change of rate is compensated for by stretching in the film.

Although each layer of the multilayer film structure may have a different thickness, the total thickness of the multilayered structure preferably ranges from about 0.3 mils (7.6  $\mu\text{m}$ ) to about 5.0 mils (127.0  $\mu\text{m}$ ) and preferably from about 0.5 mils (12.7  $\mu\text{m}$ ) to about 1.5 mils (37.5  $\mu\text{m}$ ). While such thicknesses are preferred as providing a readily flexible film, it is to be understood that other film thicknesses may be produced to satisfy a particular need and yet fall within the scope of the present invention.

The following non-limiting examples serve to illustrate the invention.

### EXAMPLES

The starting polymers used were analyzed by Gas Chromatography (GC) using standard procedures. The precision of these measurements is  $\pm 2\%$ . The films were analyzed by Differential Scanning Calorimetry (DSC) using a Seiko RDC-220 thermal analyzer, equipped with a robotics system. About 7.5 ( $\pm 0.5$ ) mg of the film sample was crimped in an aluminum pan, heated from room temperature to about 280  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}$  / min., and held there to erase crystalline memory. Subsequently, the sample was cooled from 280  $^{\circ}\text{C}$  to room temperature at a cooling rate of 10  $^{\circ}\text{C}$  and then reheated at the same rate. The  $T_m$  reported in the examples is the one obtained upon initial heating cycle, i.e., corresponding to the "as - received films" cast under the same conditions. All grades of nylons used in this study are readily commercially available.

### EXAMPLE 1

This example prepares physical blends of a copolymer of nylon 6/nylon 66 with a copolymer of nylon 6/nylon 12. Dried pellets of 50% nylon 6 (85)/nylon 66(15) and 50% nylon 6(81)/nylon 12(19) copolymers were

physically mixed in the weight percents indicated in Table 1. The compositions were dried at 82 °C for about 18 hours and then extruded through a Killion single screw extruder (D = 1.5 in; L/D = 24 / 1) equipped with three heating zones (232 °C , 257 °C and 260 °C ) and two adapters (260 °C). The melt temperature was measured as 267 °C. After passing through an extrusion film die maintained at 260 °C, the extrudate was cast on a roll maintained at 82 °C followed by a cooling roll maintained at 43 °C. The resultant film had a total thickness of about 2 mil.

10

TABLE 1

Film #	Film Description	T <sub>m</sub> , °C
1	100% N6(85)/N66(15) (control)	196.7
2	50% N6(85)/N66(15) Copolymer 50% N6(81)/N12(19) Copolymer	198.0
3	100% N6(81)/N12(19) Copolymer (control)	203.5

The melting patterns of each film are plotted in Figure 1. These data show that physical mixtures of a nylon 6/66 copolymers and a nylon 6/12 copolymer according to the invention (film 2) yields a composition having only one detectable melting point. It is clear that the blend according to the invention is homogenous and miscible in the crystalline phase, as evident by a single T<sub>m</sub>. These data are shown in Figure 1.

20

EXAMPLE 2

This example prepares physical blends of a copolymer of nylon 6/nylon 66 with a copolymer of nylon 6/nylon 12. Dried pellets of nylon 6(85)/nylon 66(15) and nylon 6(50)/nylon 12(50) copolymers were physically mixed in the weight percents indicated in Table 2. The compositions were dried at 82 °C for about 18 hours and then extruded

25

through a Killion single screw extruder ( $D = 1.5$  in;  $L/D = 24 / 1$ )  
equipped with three heating zones ( $232^{\circ}\text{C}$  ,  $257^{\circ}\text{C}$  and  $260^{\circ}\text{C}$  ) and  
two adapters ( $260^{\circ}\text{C}$ ). The melt temperature was measured as  $267^{\circ}\text{C}$ .  
After passing through an extrusion film die maintained at  $260^{\circ}\text{C}$ , the  
5 extrudate was cast on a roll maintained at  $82^{\circ}\text{C}$  followed by a cooling  
roll maintained at  $43^{\circ}\text{C}$ . The resultant film had a total thickness of about  
2 mil.

TABLE 2

Film #	Film Description	T <sub>m</sub> , °C
1	100% N6(85)/N66(15) (control)	196.7
2	75% N6(85)/N66(15) Copolymer 25% N6(50)/N12(50) Copolymer	195.3
3	100% N6(50)/N12(50) Copolymer (control)	132.0

- 5 The melting patterns of each film are shown in Figure 2. These data show that physical mixtures of a nylon 6/66 copolymers and a nylon 6/12 copolymer according to the invention (film 2) yield a composition having only one detectable melting point. It is clear that the blend according to the invention is homogenous and miscible in the crystalline phase, as
- 10 evident by a single T<sub>m</sub>. These data are exhibited in Figure 2.

EXAMPLE 3

- This example prepares physical blends of copolymers nylon 6 and nylon 66 in varying proportions. Dried pellets of nylon 6 (85)/nylon 66(15) and
- 15 nylon 6(50)/nylon 69(50) copolymers were physically mixed in the weight percents indicated in Table 3. The compositions were dried at 82 °C for about 18 hours and then extruded through a Killion single screw extruder (D = 1.5 in; L/D = 24 / 1) equipped with three heating zones (232 °C , 257 °C and 260 °C ) and two adapters (260 °C). The melt
- 20 temperature was measured as 267 °C. After passing through an extrusion film die maintained at 260 °C, the extrudate was cast on a roll maintained at 82 °C followed by a cooling roll maintained at 43 °C. The resultant film had a total thickness of about 2 mil.

TABLE 3

Film #	Film Description	T <sub>m</sub> , °C
1	100% N6(85)/N66(15) (control)	196.7
2	95% N6(85)/N66(15) Copolymer 5% N6(50)/N66(50) Copolymer	196.8
3	90% N6(85)/N66(15) Copolymer 10% N6(50)/N69(50) Copolymer	196.7
4	75% N6(85)/N66(15) Copolymer 25% N6(50)/N69(50) Copolymer	195.4 and 128
5	100% N6(50)/N69(50) Copolymer (control)	129.0 and 139.6

5 The melting patterns of each film are shown in Figure 3. These data show that physical mixtures of two nylon copolymers according to the invention (films 2 and 3) yield a composition having only one detectable melting point. By increasing the amount of copolymer II to 25% (Film 4) a single significant melting point is detected as well as a trivial melting  
10 point at 128°C. It is clear that the blends according to the invention are homogenous and miscible in the crystalline phase, as evident by a single T<sub>m</sub>. These data are shown in Figure 3.

It is clear that the blends according to the invention are homogenous and  
15 miscible in the crystalline phase as evidenced by their single significant melting points. Examples 1-3 show that the two copolymers can be blended in any proportion as long as only one or predominantly one melting peak is observed, i.e. the mixed composition fulfills the criteria for super-miscibility.

20

EXAMPLE 4

A three extruder system is constructed of 3.2 cm (1 1/4", ) Killion single screw extruders (two with L/D=24/1, and the other with L/D=30/1).



Dried pellets of 50% nylon 6 (85)/nylon 66(15) and 50% nylon 6(81)/nylon 12(19) copolymers are physically mixed and fed into the extruder with L/D= 30/1 with an extrusion profile set at 232 °C, 254 °C, and 260 °C for the heating zones 1 - 3 and 260 °C for the adapters. The melt temperature is measured at 257 °C. A maleic anhydride modified polyolefin tie resin (density: 0.88 gm/cc, melt index: 1.0 gm/10 min. at 190° C is extruded through a 3.2 cm (1 1/4") diameter Killion single screw extruder L/D=24/1 equipped with four heating zones and two adapters. The extruder temperature profiles are set at 238 ° C, 249 ° C, 260 ° C, 266 ° C for the zone 1-4 and the adapters are maintained at 266 ° C. The resulting melt temperature is 263 ° C. Polyethylene is extruded in the extruder with L/D=24/1 with an extrusion profile set at 238 °C, 252 °C, 257 °C, and 260 °C for the heating zone 1 - 4 and 260 °C for the adapters. The melt temperature is measured at 260 °C. The extrudates, after passing through a coextrusion film die kept at 260 °C, is then cast on a roll maintained at 38 °C, followed by a cooling roll set at 35 °C. The resultant film has a thickness of 25 µm. The polyethylenes used are: LDPE: low density PE - density=0.919, melt index=0.65; LLDPE: linear low density PE - density=0.920, melt index=1; MDPE: medium density PE - density=0.941, melt index=4; HDPE: high density PE - density=0.954, melt index=6. The films are exposed to the environment without restraints. No edge curl is noticed from any film. It can be seen from the foregoing that that the invention provides films having excellent curl resisting properties.

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#### EXAMPLE 5

Example 4 is repeated except the nylon used is nylon 6 homopolymer. Significant edge curl is noticed from the multilayered film produced.

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EXAMPLE 6

Example 4 is repeated except the nylon used is nylon 66 homopolymer. Significant edge curl is noticed from the multilayered film produced.

5

EXAMPLE 7

Example 4 is repeated except the nylon used is N6(85)/N66(15) copolymer. Significant edge curl is noticed from the multilayered film produced.

10

EXAMPLE 8

Example 4 is repeated except the nylon used additionally contains 2% of amorphous nylon. No significant edge curl is noticed from the multilayered film produced.

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What is claimed is:

1. A nylon composition which comprises a substantially uniform blend of at least one semi-crystalline copolymer I and at least one semi-crystalline copolymer II, wherein the proportion by weight of each of copolymer I and copolymer II is such that the composition has only one significant melting point; wherein
  - (a) copolymer I is a copolymer of a semi-crystalline nylon A and a semi-crystalline different nylon B wherein nylon A is present in copolymer I in an amount of from about 70 percent to about 95 percent by weight and nylon B is present in copolymer I in an amount of from about 5 percent to about 30 percent by weight of copolymer I; and
  - (b) copolymer II is a copolymer of semi-crystalline nylon A and at least one different semi-crystalline nylon C wherein nylon A is present in copolymer II in an amount of from about 40 percent to about 95 percent by weight and nylon C is present in copolymer II in an amount of from about 5 percent to about 60 percent by weight of copolymer II; and
  - (c) wherein nylon A and nylon B are selected from the group consisting of nylon 6 and nylon 66; and
  - (d) wherein nylon C is selected from the group consisting of nylon 9, nylon 11, nylon 12, nylon 46 and nylon 69.
2. The composition of claim 1 which has only one melting point.
3. The composition of claim 1 wherein the amount of copolymer I ranges from about 75 % to about 95% and the amount of copolymer II ranges from about 5 % to about 25 % based on the weight of the composition.
4. The composition of claim 1 wherein the amount of copolymer I ranges from about 90 % to about 93% and the amount of copolymer II ranges from about 7 % to about 10 % based on the weight of the composition.

5. The composition of claim 1 wherein the amount of nylon A in copolymer I ranges from about 75 % to about 90 % and the amount of nylon B ranges from about 10% to about 25% by weight of copolymer I.
- 5     6. The composition of claim 1 wherein the amount of nylon A in copolymer I ranges from about 80 % to about 85 % and the amount of nylon B ranges from about 15% to about 20% by weight of copolymer I.
7. The composition of claim 1 wherein the amount of nylon A in  
10     copolymer II ranges from about 50 % to about 80 % and the amount of nylon B ranges from about 30% to about 50% by weight of copolymer II.
8. The composition of claim 1 wherein the amount of nylon A in  
15     copolymer II ranges from about 50 % to about 65 % and the amount of nylon B ranges from about 35% to about 50% by weight of copolymer II.
9. The composition of claim 1 further comprising at least one non-  
20     crystalline, amorphous nylon.
10. The composition of claim 1 further comprising at least one non-crystalline, amorphous nylon in an amount of from about 1 % to about 5% based on the weight of the composition.
- 25     11. The composition of claim 1 wherein nylon A comprises nylon 6.
12. The composition of claim 1 wherein nylon A comprises nylon 66.
- 30     13. The composition of claim 1 wherein nylon C comprises nylon 69.

14. A method for producing a substantially uniform nylon composition which comprises:

(i) forming a mixture of solid particles of at least one semi-crystalline copolymer I and at least one semi-crystalline copolymer II, wherein the proportion by weight of each of copolymer I and copolymer II is such

that the composition has only one significant melting point; wherein

(a) copolymer I is a copolymer of a semi-crystalline nylon A and a semi-crystalline different nylon B wherein nylon A is present in copolymer I in an amount of from about 70 percent to about 95 percent by weight and

nylon B is present in copolymer I in an amount of from about 5 percent to about 30 percent by weight of copolymer I; and

(b) copolymer II is a copolymer of semi-crystalline nylon A and at least one different semi-crystalline nylon C wherein nylon A is present in copolymer II in an amount of from about 40 percent to about 95 percent

by weight and nylon C is present in copolymer II in an amount of from about 5 percent to about 60 percent by weight of copolymer II; and

(c) wherein nylon A and nylon B are selected from the group consisting of nylon 6 and nylon 66; and

(d) wherein nylon C is selected from the group consisting of nylon 9,

nylon 11, nylon 12, nylon 46 and nylon 69; and

(ii) melt blending the mixture at a temperature of at least the higher of the melting points of copolymer I or copolymer II.

15. The method of claim 14 wherein the mixture further comprises at least one non-crystalline, amorphous nylon.

16. The method of claim 14 wherein nylon A comprises nylon 6.

17. The method of claim 14 wherein nylon A comprises nylon 66.

18. A multilayered film structure which comprises at least one nylon composition film layer attached to at least one olefin containing polymer film layer, wherein the nylon composition film layer comprises a substantially uniform blend of at least one semi-crystalline copolymer I  
5 and at least one semi-crystalline copolymer II, wherein the proportion by weight of each of copolymer I and copolymer II is such that the composition has only one significant melting point; wherein  
(a) copolymer I is a copolymer of a semi-crystalline nylon A and a semi-crystalline different nylon B wherein nylon A is present in copolymer I in  
10 an amount of from about 70 percent to about 95 percent by weight and nylon B is present in copolymer I in an amount of from about 5 percent to about 30 percent by weight of copolymer I; and  
(b) copolymer II is a copolymer of semi-crystalline nylon A and at least one different semi-crystalline nylon C wherein nylon A is present in  
15 copolymer II in an amount of from about 40 percent to about 95 percent by weight and nylon C is present in copolymer II in an amount of from about 5 percent to about 60 percent by weight of copolymer II; and  
(c) wherein nylon A and nylon B are selected from the group consisting of nylon 6 and nylon 66; and  
20 (d) wherein nylon C is selected from the group consisting of nylon 9, nylon 11, nylon 12, nylon 46 and nylon 69.

19. The multilayered film structure of claim 18 wherein the nylon composition film layer further comprises at least one non-crystalline,  
25 amorphous nylon.

20. The multilayered film structure of claim 18 wherein the nylon composition film layer and the olefin containing polymer film layer are attached by means of an intermediate adhesive.

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21. The multilayered film structure of claim 18 wherein the nylon composition film layer and the olefin containing polymer film layer are attached by means of an intermediate adhesive which comprises at least one polyolefin having at least one functional moiety of an unsaturated carboxylic acid or anhydride thereof.
22. The multilayered film structure according to claim 18 wherein the olefin containing polymer film layer comprises one or more components selected from the group consisting of homopolymers, copolymer, and terpolymers of alpha-olefins.
23. The multilayered film structure according to claim 18 wherein the olefin containing polymer film layer comprises one or more components selected from the group consisting of ultra low density, low density, linear low density, medium density, or high density polyethylene, polypropylene, polybutylene, polybutene-1, poly-3-methylbutene-1, poly-pentene-1, poly-4-methylpentene-1, polyisobutylene, polyhexene, ethylene-propylene copolymers; ethylene-butene copolymers; ethylene-pentene copolymers; ethylene-hexene copolymers; ethylene-propylene-diene copolymers, acrylonitrilebutadiene-styrene polymers, copolymers of olefins with vinyl acetate, acrylates or methacrylates and mixtures thereof.
24. The multilayered film structure according to claim 18 wherein the at least one olefin containing polymer film layer and the at least one nylon composition layer are laminated together via an intermediate adhesive.
25. A method for preparing a multilayered film structure which comprises coextruding a molten nylon composition film layer and a molten polyolefin layer attached onto at least one side of the nylon composition film layer, through a coextrusion die, wherein the polyolefin layer

- comprises at least one olefin containing polymer; wherein the nylon composition film layer comprises a substantially uniform blend of at least one semi-crystalline copolymer I and at least one semi-crystalline copolymer II, wherein the proportion by weight of each of copolymer I and copolymer II is such that the composition has only one significant melting point; wherein
- (a) copolymer I is a copolymer of a semi-crystalline nylon A and a semi-crystalline different nylon B wherein nylon A is present in copolymer I in an amount of from about 70 percent to about 95 percent by weight and nylon B is present in copolymer I in an amount of from about 5 percent to about 30 percent by weight of copolymer I; and
- (b) copolymer II is a copolymer of semi-crystalline nylon A and at least one different semi-crystalline nylon C wherein nylon A is present in copolymer II in an amount of from about 40 percent to about 95 percent by weight and nylon C is present in copolymer II in an amount of from about 5 percent to about 60 percent by weight of copolymer II; and
- (c) wherein nylon A and nylon B are selected from the group consisting of nylon 6 and nylon 66; and
- (d) wherein nylon C is selected from the group consisting of nylon 9, nylon 11, nylon 12, nylon 46 and nylon 69.

26. The method of claim 25 further comprising casting or blowing, and optionally monoaxially or biaxially stretching the multilayered film structure.

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27. The method of claim 25 wherein the nylon composition film layer further comprises at least one non-crystalline, amorphous nylon.

28. The method of claim 25 wherein the nylon composition film layer and the polyolefin layer are attached by means of an intermediate adhesive.

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29. The method of claim 25 wherein the nylon composition film layer and the polyolefin layer are attached by means of an intermediate adhesive which comprises at least one polyolefin having at least one functional moiety of an unsaturated carboxylic acid or anhydride thereof.

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30. The method of claim 25 wherein the polyolefin layer comprises one or more components selected from the group consisting of homopolymers, copolymer, and terpolymers of alpha-olefins.

# Melting Pattern Of Nylon Copolymer Blend Films

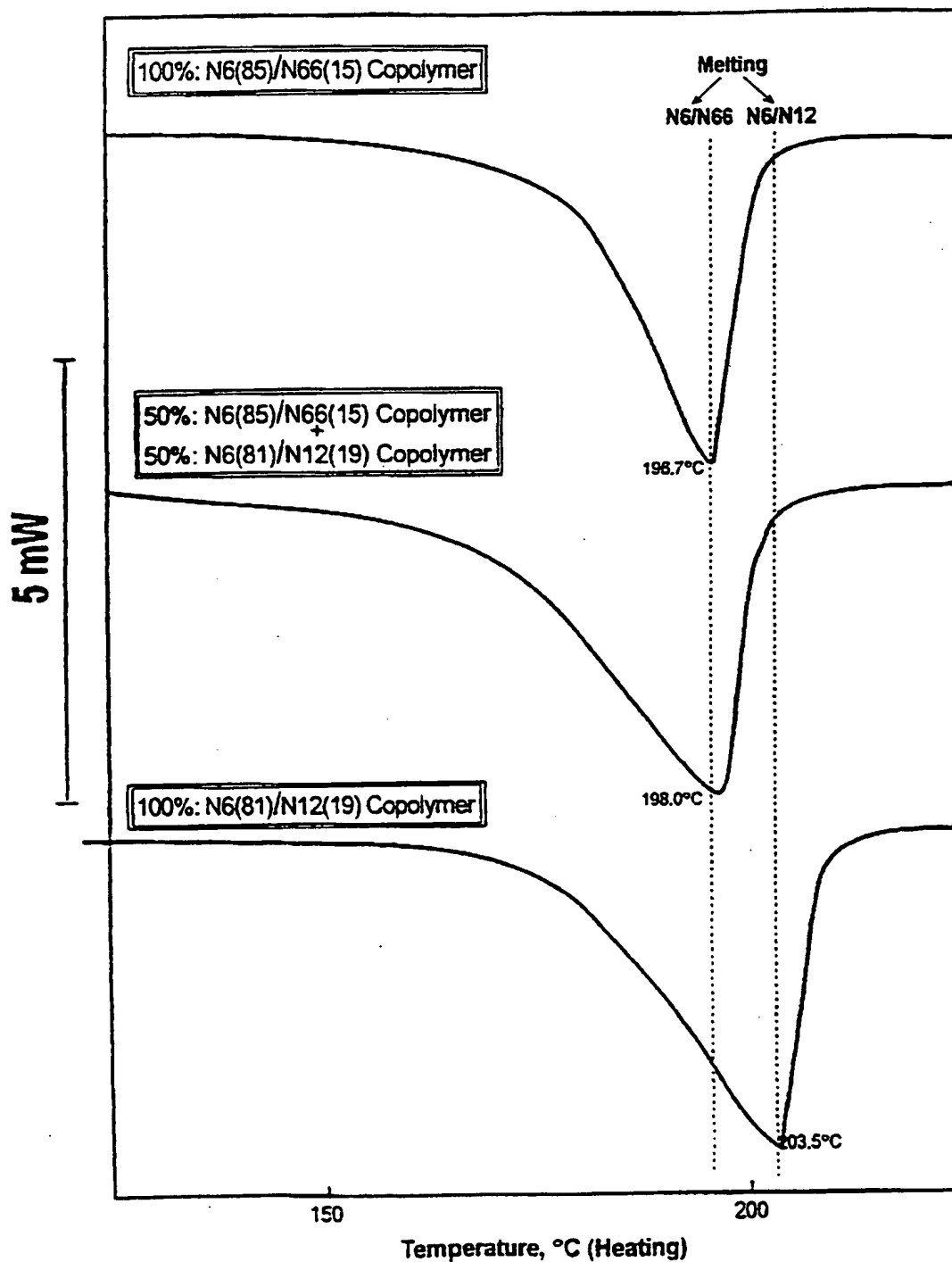


FIGURE 1

# Melting Pattern Of Nylon Copolymer Blend Films

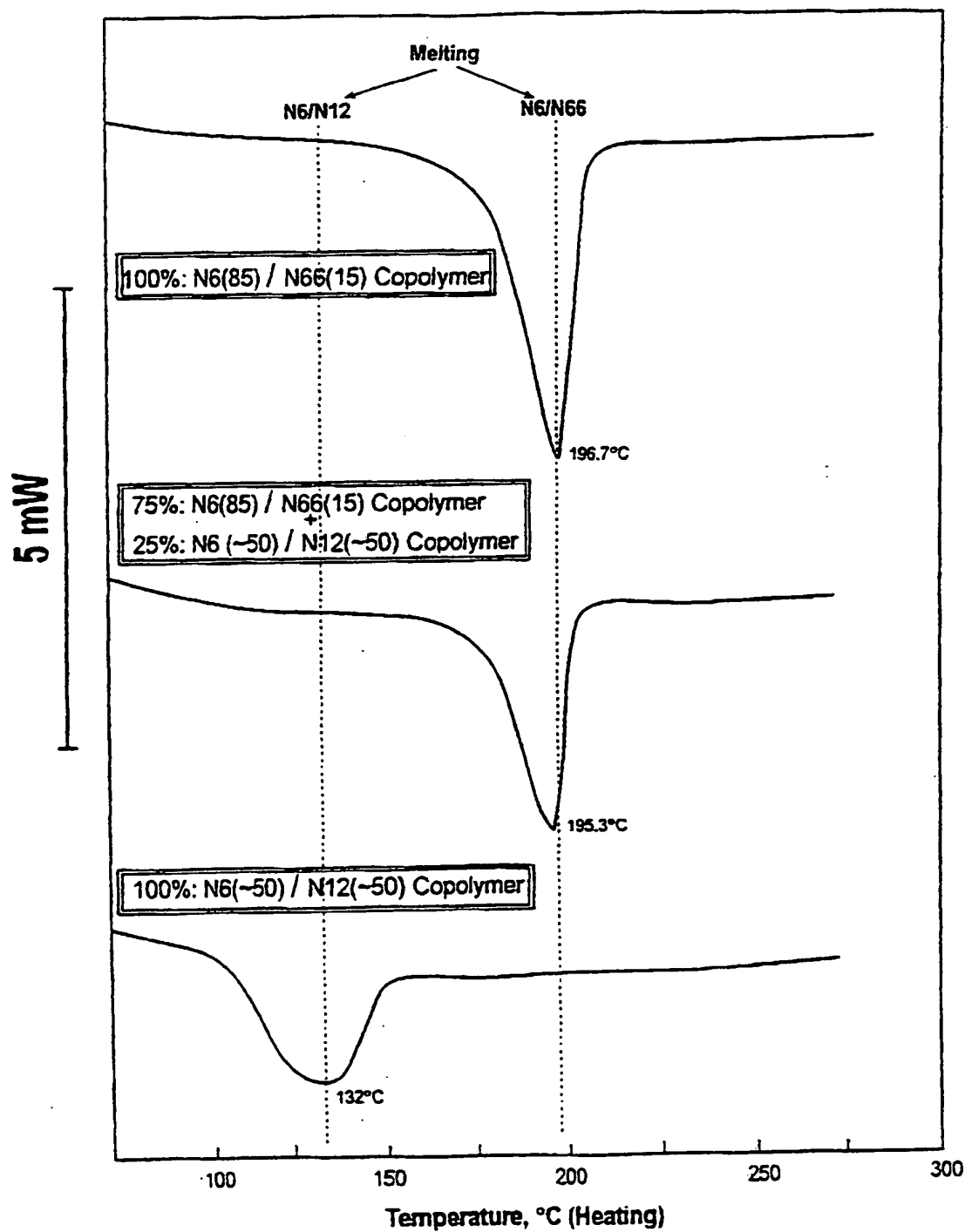


FIGURE 2

### Melting Pattern Of Nylon Copolymer Blend Films

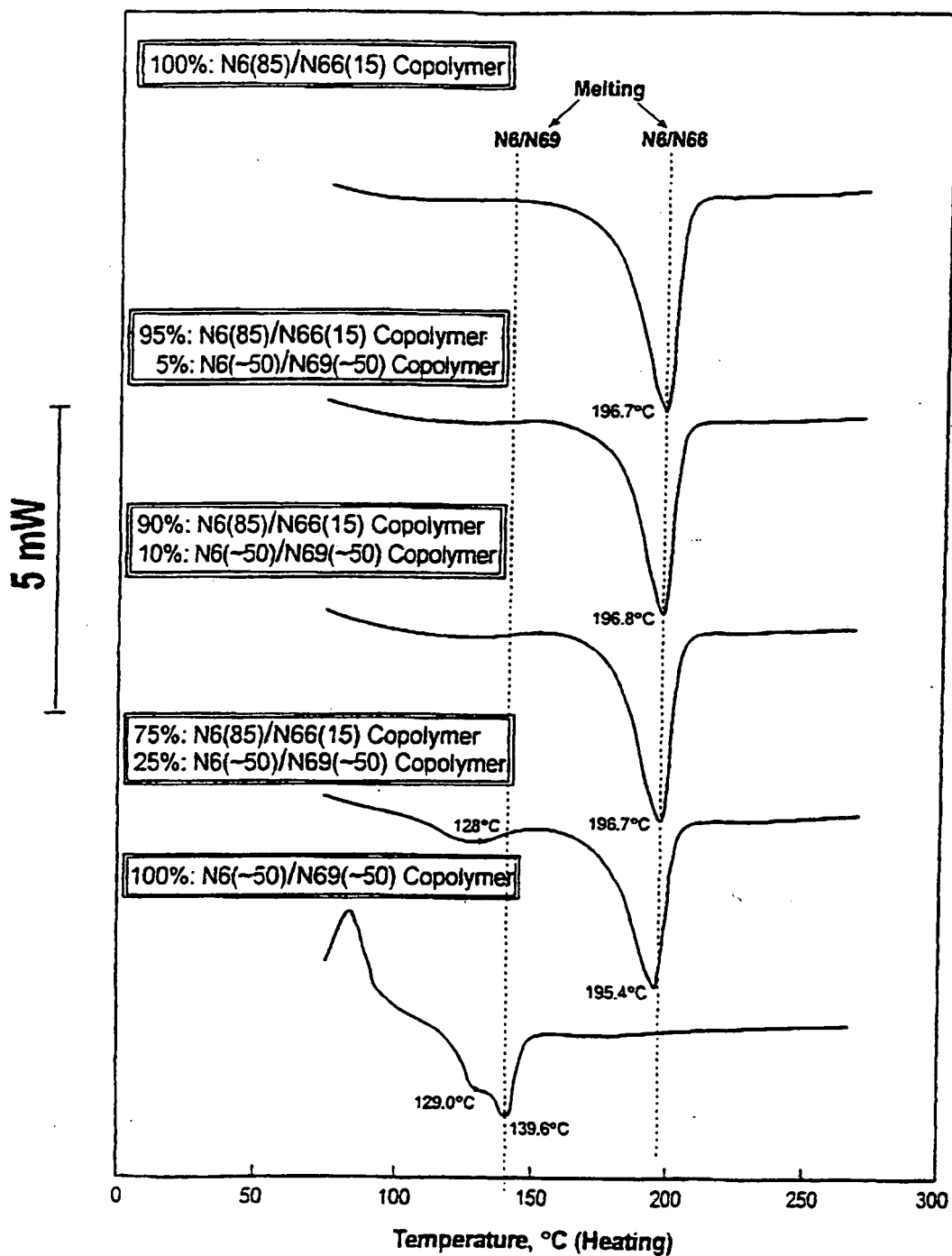


FIGURE 3

# INTERNATIONAL SEARCH REPORT

Int tional Application No

PCT/US 99/04692

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L77/00 C08L77/06 C08L77/02 B32B27/34 B32B27/08  
 //(C08L77/06,77:06),(C08L77/00,77:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 408 390 A (DU PONT CANADA) 16 January 1991 (1991-01-16) cited in the application	
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

14 July 1999

Date of mailing of the international search report

27/07/1999

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# INTERNATIONAL SEARCH REPORT

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PCT/US 99/04692

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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